

## Magnetic order and spin fluctuations in Ni-rich $\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_2$

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### Abstract

The crystal and magnetic structures of polycrystalline  $\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_2$  were studied by AC magnetic susceptibility and neutron powder diffraction. The Ni-rich compound crystallizes with rhombohedral symmetry belonging to the space group  $R\bar{3}m$ . The AC magnetic susceptibility reveals antiferromagnetic interactions between the Ni moments. Two distinct magnetic components were seen in the magnetic diffraction pattern. One is associated with the ordering of the Ni ions, whereas the other originates from the intra-layer short-range correlations of the Ni ions located on the Li sites. Ni moments order below 180 K, with a saturated moment of  $\langle \mu_z \rangle = 1.70(8)\mu_B$ .  
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The crystalline structure of  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  has been reported in several studies [1–4]. In the compounds with low Li concentrations, the original NiO cubic rock-salt structure is preserved, and the Li ions preferentially enter the face center sites. When more Li ions are incorporated into the system, they form a lamellar structure along the (1 1 1) crystallographic direction [3], and the system transforms into a hexagonal structure as  $x$  reaches 0.62. For  $\text{LiNiO}_2$ , the crystalline structure may be viewed as an alternate stacking of triangular Li layers and triangular Ni layers separated by O ions, so that the Ni moments form a two-dimensional triangular magnet [5]. Mertz et al. [6] introduced a percolation model to describe the formation of Ni clusters and used an Ising model to calculate the magnetic behavior. With this model, they successfully predicted the occurrence of a superparamagnetic to ferromagnetic transition at  $x = 0.864$ , which agrees well with the observation. Recently, Chung et al. [7] pointed out that the local Jahn–Teller distortion and orbital ordering

are responsible for the unconventional magnetic behavior. In this article, we report on the results of studies made on the magnetic properties of a compound near the superparamagnetic to ferromagnetic regime.

A polycrystalline sample of  $\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_2$  was prepared by solid-state reaction techniques. Stoichiometric mixtures of  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{Ni}(\text{OH})_2$  powders were thoroughly ground and heated at 800 °C for 12 h, in a flowing oxygen atmosphere at a rate of 0.21/min, followed by slowly cooling to room temperature. Crystal and magnetic structures were studied by neutron powder diffraction. The neutron diffraction experiments were performed at the NIST Center for Neutron Research, and the data were collected on the BT-1 and BT-9, for the crystalline and magnetic studies, respectively. The AC magnetic susceptibilities were measured using a weak driving field, with an RMS strength of 1 Oe and a frequency of 100 Hz.

In Fig. 1, we show the observed and refined high-resolution neutron powder diffraction pattern taken at 300 K. This pattern was analyzed using the GSAS program [8], following the Rietveld method. The analysis shows that 14% of the Li sites were occupied by Ni ions, whereas 4% of the Ni sites appeared to be Li ions, as indicated in

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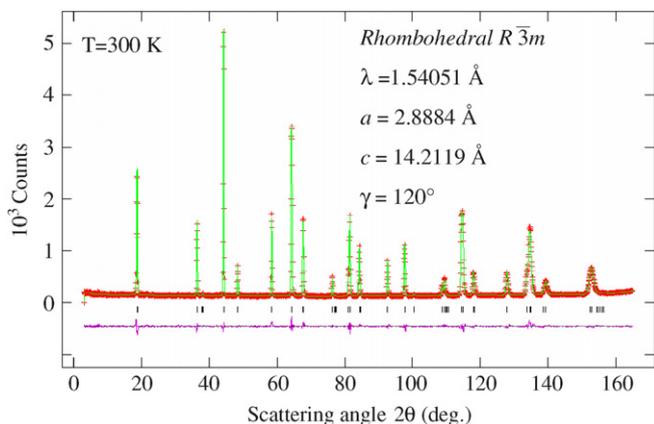


Fig. 1. Plot of the observed (crosses) and fitted (solid lines) neutron powder diffraction pattern taken at 300 K. The compound crystallizes into a rhombohedral symmetry of space group  $R\bar{3}m$ .

Table 1

List of the refined structural parameters of  $\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_2$  at 300 K, where  $R_p$ ,  $R_{wp}$ , and  $\chi$  represent the goodness factors

$\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_2$ , rhombohedral  $R\bar{3}m$ , 300 K

$a = b = 2.8884(2) \text{ \AA}$ ,  $c = 14.2119 \text{ \AA}$

$\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$

Name	X	Y	Z	B ( $\text{\AA}^2$ )	
Occupancy					
Li(1)	0	0	0	2.50(9)	0.860(3)
Ni(1)	0	0	0	2.50(9)	0.140(3)
Li(2)	0	0	0.5	0.58(4)	0.040(7)
Ni(2)	0	0	0.5	0.58(4)	0.960(2)
O	0	0	0.24259(8)	0.96(5)	1.00(4)
$R_p = 4.79\%$		$R_{wp} = 6.54\%$		$\chi = 1.76$	

Table 1, where the refined structural parameters are listed. The compound was also found to be fully oxygenated. The chemical composition that we obtained from the fit was thus  $\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_3$ , which agrees well with the stoichiometric composition.

Fig. 2 shows the temperature profiles of the in-phase component  $\chi'$  of AC susceptibility, measured at an applied magnetic field of 0 and 1 T. The main feature is the sharp peak at 130 K, signaling the occurrence of Ni ordering. An applied magnetic field of 1 T strongly suppresses the magnetic response. However, the peak is still evident, and shifts to a higher temperature, indicating antiferromagnetic coupling of the Ni moments.

Shown in the inset to Fig. 2 is the temperature dependence of  $1/\chi'$ . Both plots depart from the Curie–Weiss linear dependence at 180 K, showing the appearance of magnetic correlations below this temperature, and an applied magnetic field of 1 T does not significantly alter the paramagnetic state. The Curie–Weiss temperature that we obtained from the fit was +155 K, indicating the presence of ferromagnetic interactions between the Ni moments.

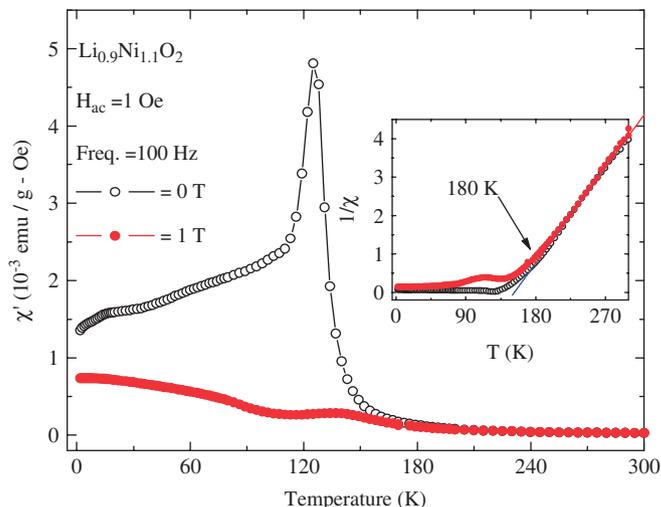


Fig. 2. Plots of the variations in AC susceptibility with temperature, measured at 0 and 1 T. Shown in the inset is the temperature dependence of the reciprocal susceptibility.

Neutron magnetic diffraction measurements were then carried out to explore the magnetic structure of the Ni spins. Shown in Fig. 3 is the magnetic diffraction pattern at 35 K, obtained by subtracting the diffraction pattern taken at 200 K, which serves as the non-magnetic background. Two distinct magnetic components may be distinguished from the pattern shown in Fig. 3. A series of six resolution-limited peaks that can be indexed with the nuclear unit cell demonstrates the occurrence of a long-range order of the Ni moments. A much broader peak, centered at  $2\theta \approx 46^\circ$ , shows the existence of short-range correlations as well.

The short-range correlations are most likely to be magnetic in this compound. One possible origin is that it is associated with the correlations among those Ni ions that enter the Li sites. These intra-layer correlations begin to develop below  $\sim 100$  K, judging from the fact that there is no such scattering in the 100 K magnetic diffraction pattern and from the appearance of an additional increase in  $\chi'$  below 100 K, which is seen in the  $H = 1$  T data shown in Fig. 2. We estimate that the length scale of the short-range order is  $\sim 6 \text{ \AA}$  at 35 K. For the long-range Ni ordering, no  $\{001\}$  intensity was observed, signaling that the moment direction is predominantly along the  $c$  crystallographic axis direction. Fig. 4 shows the temperature dependence of the  $\{010\}$  peak intensity, showing an ordering temperature of  $T_N \approx 180$  K for the Ni moments, which corresponds to the temperature at which  $\chi'$  departs from the Curie–Weiss behavior, as shown in the inset to Fig. 2.

Based on our observations, we propose the following magnetic behavior for the Ni ions in Ni-rich  $\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_2$ . The Ni moments begin to order below 180 K, where the inter-Ni-layer correlations are coupled through the Ni ions located on the Li sites (14% for the present compound), with both ferromagnetic and antiferromagnetic couplings for the Ni ions in the adjacent layers. The spin orientation of the Ni ions that fits the observed pattern is shown in

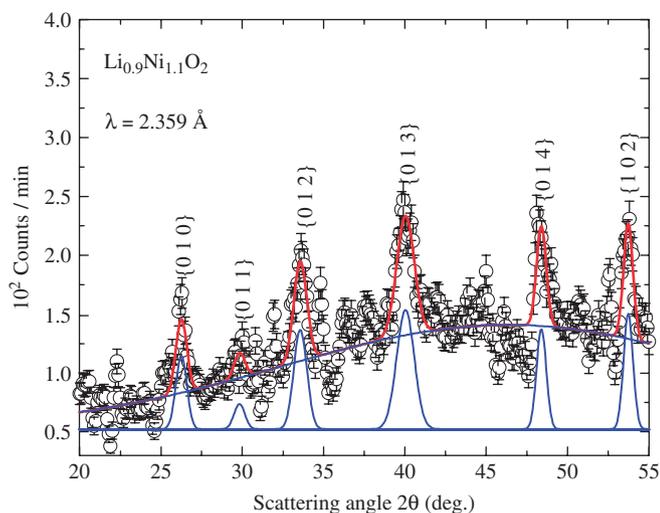


Fig. 3. Magnetic diffraction pattern taken at 35 K, where six resolution-limited peaks and a broad one are evident.

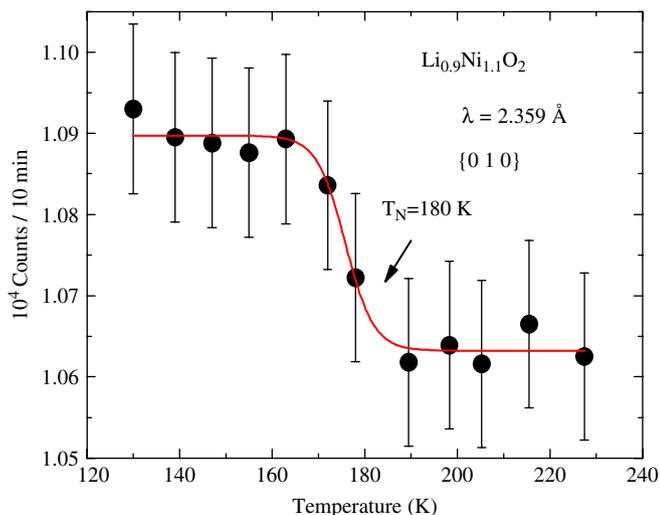


Fig. 4. Plot of the temperature dependence of the {010} peak intensity, showing an ordering temperature of  $T_N \sim 180$  K for the Ni moments.

Fig. 5. The calculated pattern based on the proposed model is shown as solid lines in Fig. 3, which agrees reasonably well with the observed pattern. The Ni moments become saturated below 160 K, with a saturated moment of  $\langle \mu_z \rangle = 1.72(8)\mu_B$ . Below 100 K, the correlations among

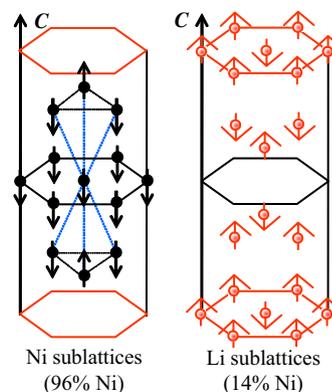


Fig. 5. Plot of the proposed spin configuration of the Ni moments in  $\text{Li}_{0.9}\text{Ni}_{1.1}\text{O}_2$ .

the Ni ions located in the Li layers begin to develop, and this intra-layer correlation length reaches  $6 \text{ \AA}$  at 35 K. We finally remark that the existence of both the ferromagnetic and antiferromagnetic interactions in this class of materials is believed to be associated with the complicated  $\text{Ni}^{3+}\text{-O-Ni}^{3+}$  and  $\text{Ni}^{2+}\text{-O-Ni}^{3+}$  interactions [9].

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